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THE EFFECT OF COMPOSITION AND SYNTHESIS CONDITIONS ON THE STRUCTURE OF COBALT-BEARING PIGMENTS OF THE SPINEL TYPE

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The results of producing cobalt-bearing spinels of a blue-sky to blue color range by self-propagating high-temperature synthesis (SHS) are described. The effect of the conditions of synthesis and the mixture composition on the structure of compounds obtained is demonstrated. The SHS method makes it possible to obtain spinels that can be used as ceramic pigments.

One of the methods for producing pigments of the spinel type for ceramic paints and glazes is self-propagating high-temperature synthesis (SHS). It is based on using the heat from exothermic reactions and is faster and more cost-efficient than traditional methods.

The purpose of the present paper is to obtain pigments of the spinel type by SHS and to study the effect of the initial composition and conditions of synthesis on the structure formation processes.

Pigments were synthesized using Al_2O_3, Co_2O_3, ZnO, MgO, and aluminum powder ASD-4. Synthesis was performed in a constant-pressure plant in an argon atmosphere and in air. The obtained pigments were identified by x-ray phase analysis on a DRON-UM1 diffractometer (filtered CoK_α radiation) and infrared spectroscopy in the range of $1400 - 400\ cm^{-1}$ on a Nicolet 5700 IR-Fourier diffractometer with a diffuse reflection device in KBr. The microstructure of samples was studied using light microscopy (Axiovert 200M).

Blue pigments were obtained in the $CoO - Al_2O_3$ system. According to the x-ray phase analysis data, the products of synthesis performed in the argon atmosphere contain, besides aluminocobalt spinel $CoAl_2O_4$, also a substantial amount of corundum (Al_2O_3). Furthermore, the products contain metallic cobalt and $Co(AlO_2)_2$. The IR spectroscopic analysis[2] indicates the formation of a mixed spinel (Fig. 1, curve *1*) in the system, since in addition to the octahedral aluminum atom $[AlO_6]$ whose vibrations are manifested at $560.0\ cm^{-1}$, which is typical of normal spinels, we observed also absorption bands of the tetrahedral atom $[AlO_4]$ at $624.5\ cm^{-1}$, which is present in inverse spinels. Moreover, there is an intense absorption band at $1088.9\ cm^{-1}$ related to the vibrations of the ion $(AlO_2)^-$ [1 – 3].

Synthesis performed in the air atmosphere produces pigments with better color characteristics, which is directly related to their composition and structure. The modification of the structure is clearly visible in the IR spectra of the pigments. Thus, the absorption bands at 886.1, 979.5, and

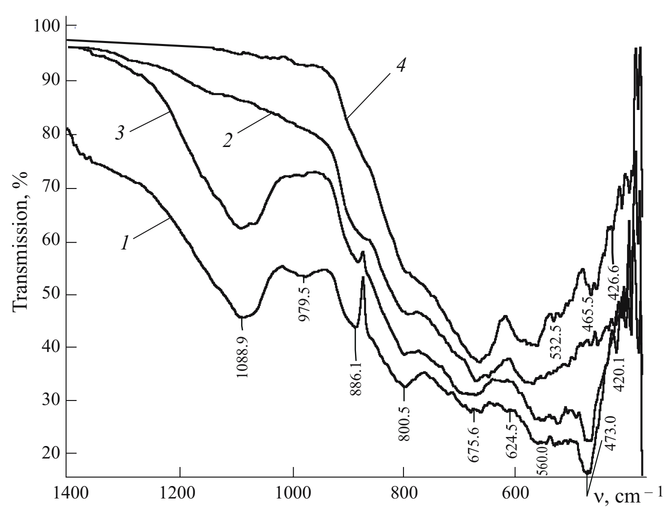

Fig. 1. IR spectra of pigments: *1*) SK (system $CoO - Al_2O_3$), argon; *2*) SK (system $CoO - Al_2O_3$), air; *3*) UKTs-2 (system $ZnO - CoO - Al_2O_3$), $NaNO_3$; *4*) UKTs-2 (system $ZnO - CoO - Al_2O_3$), air.

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[2] IR spectroscopy analysis was carried out on the equipment of the Scientific Analytic Center of the Tomsk Polytechnic University.

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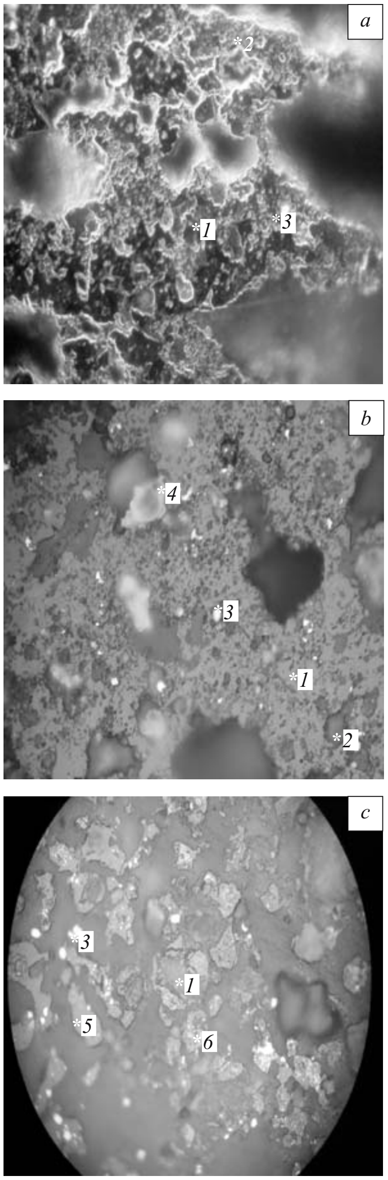

Fig. 2. Microstructure of synthesized pigments at magnification × 120 (*a*, *b*) and × 50 (*c*): *1*) aluminocobalt spinel; *2*) aluminozinc spinel; *3*) metallic cobalt; *4*) sodium aluminate; *5*) alumino-magnesian spinel; *6*) triple eutectic.

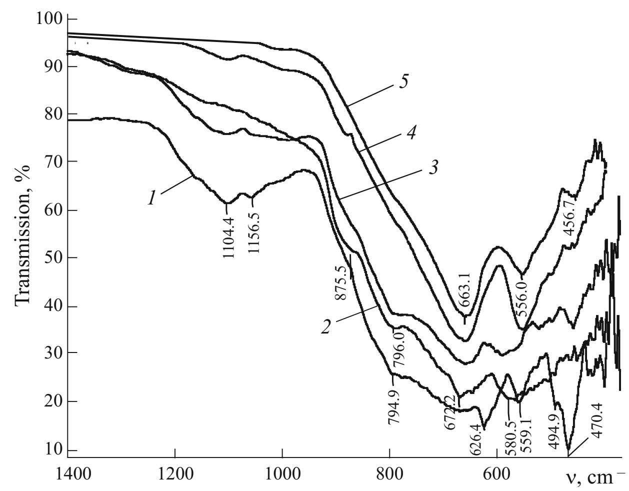

Fig. 3. IR spectra of pigments obtained in systems: *1*) ZnO – CoO – Al_2O_3 (deficit of cobalt); *2*) CoO – Al_2O_3 (pigment SK); *3*) ZnO – CoO – Al_2O_3 (pigment UKTs-2); *4*) MgO – ZnO – CoO – Al_2O_3 (pigment UKTsM-2), $MgNO_3 \cdot 6H_2O$; *5* – ZnO – CoO – Al_2O_3 (pigment UKTs-3), ZnO content higher than in pigment UKTs-2, $NaNO_3$.

1088.9 cm^{-1} determined by the vibrations of the link ν(Al – O) in Al_2O_3 and in the ion $(AlO_2)^-$, respectively, disappear in the CoO-Al_2O_3 system (Fig. 1, curve *2*). The peak at 473.0 cm^{-1} typical of corundum decreases perceptibly as well [4, 5].

Similar results were obtained in the system ZnO – CoO – Al_2O_3. The study of the microstructure of this system indicates the presence of two types of spinel (aluminocobalt and aluminozinc), as well as a small amount of metallic cobalt in the product (Fig. 2*a*). At the same time, the increased quantity of ZnO changes the pigment color to a lighter shade. The formation of aluminozinc spinel is also corroborated by IR spectroscopy data. Thus, vibrations of tetrahedral zinc $[ZnO_4]$ are registered in the considered product at 532.5 and 465.5 cm^{-1} (Fig. 1, curve *4* and Fig. 3, curve *5*) [1, 3, 6]. Upon introducing ZnO and MgO, the quantity of free Al_2O_3 in the products of synthesis decreases, and zinc and magnesium spinelides are formed. Thus, the peak at 886.1 cm^{-1} related to stretching vibrations of the bond ν(Al – O) in Al_2O_3 virtually disappears (Fig. 3, curves *3* and *5*)

The initial composition of the mixture has a significant effect on the chromaticity of synthesized pigments, since in the case of Co_2O_3 deficit a mixed spinel is formed. Along with aluminocobalt spinel that typically has vibrations of bonds ν(Al – O) in $[AlO_6]$ and ν(Co – O) in $[CoO_4]$ at 559.1 and 672.2 cm^{-1}, respectively, we observe the stretching and deformation vibrations of the bonds of corundum at 794.9, 470.4, and 420.1 cm^{-1}. Furthermore, the absorption band ν(Al – O) of the tetrahedrally coordinated aluminum atom at 626.4 cm^{-1} is present, which is typical of an inverse spinel (Fig. 3, curve *1*). The pigment has a gray-blue color.

To intensify the process, the synthesis was carried out with strong oxidizers: $Mg(NO_3)_2 \cdot 6H_2O$ and $NaNO_3$ (RF patent No. 2121463). As a result of adding $NaNO_3$, the salt $NaAlO_2$ is formed, whereas the quantity of metallic cobalt actually does not decrease. X-ray phase analysis corroborates this fact. The IR spectra show a perceptible peak at 1088.9 cm^{-1} typical of the vibrations of the bond of the ion $(AlO_2)^-$ (Fig. 1, curve *3*). The study of the microstructure of the product corroborates the presence of sodium aluminate in the salt composition (Fig. 2*b*). The replacement of $NaNO_3$ by $Mg(NO_3)_2 \cdot 6H_2O$ gives better results. Along with aluminocobalt spinel, we identified the presence of alumomagnesial spinel and the persistence of the metallic cobalt inclusion; the area of a low-melting triple eutectic was regis-

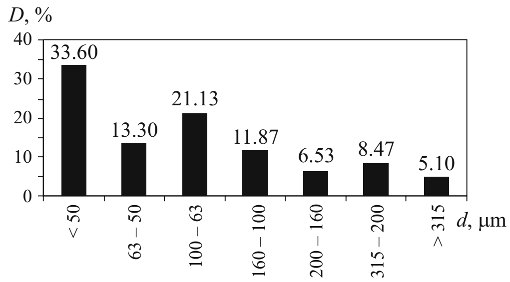

Fig. 4. Histogram of dispersion distribution of pigment UKTs-2 obtained by SHS method [*D*) weight part of powder that has passed through a sieve with prescribed cell sizes as a ratio of the total weight of screened material; *d*) cell size].

tered (Fig. 2*c*, system MgO – CoO – Al_2O_3). Depending on the MgO content in the initial batch, the pigment color varies from blue to bright blue.

The pigments obtained by SHS in the systems ZnO – CoO – Al_2O_3, MgO – CoO – Al_2O_3, and MgO – ZnO – CoO – Al_2O_3 are finely dispersed and do not require additional milling. Thus, screening the pigment UKTs-2 on sieves (system ZnO – CoO – Al_2O_3) we found that the fraction with the size of spinel particle below 50 μm is prevalent (Fig. 4).

Thus, pigments of the blue-sky-blue range have been produced by the SHS method. Adding ZnO and MgO decreases the content of free Al_2O_3 in the system and leads to the formation of zinc and magnesium spinelides, which yields pigments of brighter and more intense shades. A partial replacement of MgO by $Mg(NO_3)_2 \cdot 6H_2O$ intensifies the processes and enables one to perform synthesis at lower temperature due to the formation of low-melting triple eutectics. The addition of $NaNO_3$ as an oxidizer is undesirable, since it leads to the formation of sodium aluminate, which impairs coloring. Pigments with the best color characteristics are synthesized in an air atmosphere.

The SHS method ensures the production of spinels that can be used as ceramic pigments.

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